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NATIONAL BUREAU OF STANDARDS REPORT

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THE USE OF ANHYDROUS METHYL ALCOHOL IN REFRIGERANT 12 AND 22 SYSTEMS

by

Paul R. Achenbach
C. W. Phillips

Report to
Mechanical Engineering Division
Headquarters, Quartermaster Research and Engineering Command
Natick, Massachusetts



U. S. DEPARTMENT OF COMMERCE
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to

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U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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THE USE OF ANHYDROUS METHYL ALCOHOL IN REFRIGERANT 12 AND 22 SYSTEMS

by

Paul R. Achenbach and C. W. Phillips

Abstract

An investigation was made relative to the use of anhydrous methyl alcohol as an antifreeze agent in refrigerating systems employing Refrigerants 12 and 22. The investigation included a review of the literature, a limited amount of laboratory work on the miscibility of methyl alcohol, water, Refrigerants 12 and 22 and refrigerant grade oil, and a survey of technical information and policy of manufacturers of refrigerating equipment, refrigerants, and desiccants. Information received in the survey indicated that five out of six manufacturers of refrigerators who have experimented with the use of one percent or less of methyl alcohol in R-12 and R-22 systems indicate satisfactory performance providing the moisture content in the system is kept at a very low level. Some of these manufacturers state that the discoloration and corrosion of metals is measurable but not objectionable under these conditions. Two of the six manufacturers now use 1/2 percent or less methyl alcohol regularly in relation to the weight of refrigerant in these domestic refrigerators and one other uses small amounts in one of their home freezer models. One large manufacturer of R-12 and R-22 refrigerants states that the use of methyl alcohol by manufacturers in amounts of one percent or less of the weight of refrigerant is acceptable based on sealed tube laboratory tests of such mixtures. There is general agreement that the use of methyl alcohol in larger amounts in R-12 and R-22 systems will cause excessive corrosion with or without the presence of water and that the initial moisture content of such systems should be kept at 25 ppm or lower regardless of whether methyl alcohol is used or not. Limited experimental data indicate that the moisture limit in R-12 and R-22 systems with regard to corrosion is probably between 100 ppm and 300 ppm of water without methyl alcohol being present. Thus in a system without an antifreeze, freezeup at the expansion device serves as a warning against conditions that might produce corrosion. With as little as 0.2 percent methyl alcohol in a system the moisture content could exceed the corrosion limit many fold before a

freezeup would furnish a warning of excessive moisture. Since a little methyl alcohol can prevent freezing in a system containing considerable moisture the report recommends that domestic refrigerators of all types and models be dehydrated at the factory to a moisture content not to exceed 25 ppm. On the assumption that thermally-sealed hermetic systems are not usually serviced in the field, their useful life with respect to the effects of moisture is largely determined by the initial condition created at the factory and the length of time they remain leak tight. For such systems it is recommended that the factory use of one percent methyl alcohol or less in relation to the weight of the refrigerant be considered acceptable. Since service operations can be performed in mechanically-sealed hermetic systems and open systems and since such operations are anticipated by their construction, it is recommended that the use of methyl alcohol in such systems be prohibited. It is further recommended that research be initiated to find a suitable method of determining the alcohol and moisture contents of new refrigerators as a part of the inspection procedures and to study the effects of moisture and anti-freezes in refrigerating systems as a basis for better specification requirements.

I. INTRODUCTION

In response to a request from the Quartermaster Research and Engineering Command, dated March 13, 1958, an investigation was made regarding the use of anhydrous methyl alcohol in refrigerating systems using Refrigerants 12 and 22. The investigation was directed primarily, but not exclusively, to the use of alcohol in the hermetic systems of domestic refrigerators. Answers were desired to the following questions:

- a. Is the exclusion of alcohol from such refrigerating systems scientifically tenable?
- b. What is the quantitative maximum of alcohol allowable without incurring injurious acid and corrosion levels?
- c. How can effective dehydration of the system at the factory prior to the addition of alcohol be determined if the limited addition of alcohol were permitted?
- d. What test method can be used to determine the moisture content of a system containing refrigerant, oil, and alcohol?
- e. At what refrigerant temperatures, if any, might the addition of alcohol be desirable?

II. PROCEDURE

The procedure used in this investigation consisted of the following steps:

1. Review of published literature on the subject of corrosion of the materials in refrigerating systems as a result of moisture, alcohol, or both.
2. A survey of expert opinion from the manufacturers of domestic refrigerators, refrigerants, driers, refrigerant oils, desiccants, and other refrigerating equipment and individuals with special information related to the problem.
3. A limited laboratory study of the miscibility of refrigerant 12, methyl alcohol, water, and refrigerant oil.

In surveying the opinion and experience of manufacturers and selected individuals, information was asked on the following questions:

1. Does methyl alcohol in quantities of one percent or less in refrigerant 12 or 22 systems cause corrosion either by itself or when combined with water over a long period of time under typical operating conditions?
2. What is the moisture limit in R12 and R22 systems with regard to corrosion of iron, copper, and aluminum?
3. What is the moisture limit in R12 and R22 systems with regard to deterioration of the hermetic motor insulation?
4. If the use of methyl alcohol were permitted in new systems, what should the limit be?
5. If methyl alcohol were permitted in new systems, how could the purchaser know that the initial dehydration of the system was thorough?

6. Would methyl alcohol and R12 or R22 remain mixed in a refrigerant charging tank if mixtures were prepared in large quantities in a manufacturer's plant?
7. Would the methyl alcohol and any water present in a system tend to accumulate in the evaporator, or would the oil circulation tend to return it to the compressor?
8. Has your company done research on the corrosive effect of methyl alcohol in refrigerating systems?
9. Does your company have an opinion or a policy for or against use of methyl alcohol in new hermetic refrigerating systems for operation at evaporator temperatures of zero F?

This inquiry was sent to the following companies and individuals:

Davison Chemical Company
Ansul Chemical Company
E. I. DuPont de Nemours & Company, Inc.
General Chemical Division, Allied Chemical and
Dye Corporation
Dow Chemical Company
Highside Chemicals Company
Admiral Corporation
General Electric Company
Amana Refrigeration, Inc.
Frigidaire Division, General Motors Corporation
Hotpoint Company
Kelvinator Division, American Motors Corporation
Norge Division, Borg-Warner Corporation
Philco Corporation
Servel, Inc.
Westinghouse Electric Corporation
Whirlpool-Seeger Corporation
Copeland Refrigeration Corporation

Carrier Corporation
Frick Company
York Division, Borg-Warner Corporation
Tenney Engineering, Inc.

H. F. Spoehrer, Sporlan Valve Company
J. F. Butterworth, Socony Vacuum Oil
W. O. Walker, University of Miami

III. RESULTS OF SURVEY OF MANUFACTURERS AND OTHERS

Question 1

Does methyl alcohol in quantities of 1% or less in Refrigerant 12 or 22 systems cause corrosion either by itself or when combined with water over a long period of time under typical operating conditions?

--- E. I. DuPont de Nemours & Company ---

"Based on laboratory tests and industry experience, it appears that methanol in amounts of one percent or less based on refrigerant is acceptable in systems using 'Freon-12' or 'Freon-22' refrigerants. However, larger amounts, especially in systems containing aluminum, should not be used. The methanol problem lies with its uncontrolled use in field service.

"Some manufacturers of refrigeration compressors regularly add methanol in amounts up to about one percent by weight based on the refrigerant. Experience with this procedure over a period of years has been good. Apparently, the use of methanol under these conditions with strict manufacturing control is not harmful. Units produced by these manufacturers are warranted for the same periods of time as others who do not use methanol. Limited laboratory tests tend to confirm the conclusion that small amounts are acceptable. In tests at 250°F for 115 days, the effect of one percent methanol was not significant (Refrig. Eng. 65, 40, Nov. 1957)."

-- Ansul Chemical Company --

"The most recent information available to us is published by DuPont which shows that Freon-22 stored in sealed glass tubes containing 1% by weight methanol and in contact with copper, iron and refrigeration grade oil will show very little decomposition at temperatures of 250° and 300°F.

"We have always taken the stand that no methanol should be used since even anhydrous alcohol will introduce moisture into the system in which it is used. Furthermore methanol itself is quite a reactive compound and can readily react with the component parts of the system, especially in the case of aluminum in which case trimethyl aluminum can be formed. Again, if a drier or dehydrator is in use in the system, the desiccant can adsorb the methanol thereby reducing its capacity for water."

-- E. W. McGovern, DuPont Company --

"Antifreezes, such as methyl alcohol, act merely as anti-freezes--they do not prevent other moisture effects, such as corrosion. As a matter of fact, methyl alcohol itself, when mixed with a dry halogenated hydrocarbon refrigerant, produces a slightly corrosive mixture."

-- Highside Chemicals Inc. --

"The test data which we have been able to locate indicate that the use of methyl alcohol in quantities of 1% or less does cause some corrosion over long periods of time."

-- Westinghouse Electric Corporation --

"Westinghouse does not use any type of anti-freeze in refrigerator compressors. We have run laboratory tests using methyl alcohol and have entered into discussions and compared test results with others on many occasions. The answers to your questions, however, are based on experience with these tests and are not the result of long-term field experience."

"I do not think that methyl alcohol in quantities of one per cent or less in refrigerant 12 systems will cause corrosion either by itself or when combined with water over a five or ten year period of time under typical operating conditions. This refers to one per cent by weight of the refrigerant. We have had no experience with alcohol in refrigerant 22 systems."

-- Whirlpool Corporation --

"We do not use methyl alcohol in our system as it serves no purpose as we have no 'freezeups'."

"We feel that alcohol serves no useful purpose and offers another element to the chemical stability problem and, therefore, should not be used."

-- Admiral Corporation --

"Results from extended life tests on units having one percent of alcohol indicate that the amount of corrosion on components is dependent to a great extent on the operating pressures and temperatures. Extensive copper plating was deposited on bearing surfaces in approximately six months on those units operating under accelerated test conditions of 235# head pressure and 250° motor winding temperatures. Similar units having a small fan in the circuit to maintain compressor housing temperatures below 150°F were comparatively free of plating after 12 months operation..

"At the present time Admiral does not use alcohol in refrigeration systems since we use Tecumseh compressors and addition of alcohol to a system automatically voids the Tecumseh warranty."

-- Kelvinator Division --

"We have been successfully employing methanol for over twenty years as an additive to refrigerant 12 for the purpose of preventing freez-up at the capillary inlet to the lowside. We have experienced no trouble relating to corrosion or compressor breakdown due to methanol, and our compressors and systems have been in continuous operation for the same length of time in the field.

We use less than 1% methanol in our refrigerant; actually, it is less than 0.5%. We have never found it necessary to use methanol in refrigerant 22 to prevent freez-up. At no time has corrosion been found to be a factor even under twenty years of typical operating conditions in the field."

-- Hotpoint Company --

"The answers given herein will be based on experience with only one refrigerant; namely, R-12 or F-12 as you choose. Answers are given under the same numbers as your questions.

"1. Extended life tests (Hotpoint units with Kelvinator Compressors) on operating systems with less than 1% alcohol have shown no signs of corrosion. These tests included units with greater than 1% alcohol and to date, they have not shown any evidence of corrosion. These tests are still in progress. These tests included units with normal and excessive quantities of moisture also."

-- Frigidaire Division --

"Methyl alcohol in quantities of 1% or less in R-12 or R-22 systems over long periods of time can cause visible corrosion and staining and iron and copper compound formation. If similar systems are test-run side by side, one dry and one with 1/2 to 1% methanol, the alcohol system can always be picked out as having more stain, corrosion, copper plating, and debris on fine filter screens than the dry system. However, for proper perspective, it does not necessarily follow that alcohol may never be used. There have been and are many instances of practical use of alcohol.

"Household refrigerators and vertical food freezers have a dry desiccant which is CaSO_4 (special coating). We have found other desiccants very satisfactory but are using this one at the present.

"Ice cream cabinets and horizontal food freezers are charged with 3 c.c. of methanol.

"We have a substantial knowledge on the rate and amount of corrosion on a methanol charged system when quantities are excessive. However, excellent statistical results as to performance and life have been obtained with a 'minimized' methanol charge of 3 cubic centimeters."

-- Norge Division --

"With the advent of aluminum tubing and evaporator assemblies for household systems the use of liquid desiccants is a greater hazard than ever before. The corrosion potential is increased many times and Norge does not recommend its use under any circumstances."

-- Copeland Refrigeration Corporation --

"We recommend that nothing be put into a hermetic refrigeration system except pure refrigerant, refrigerating oil and a suitable dehydrating agent - such as activated aluminum, Silica Gel, Molecular Sieve, etc., (no liquid dehydrants.)

"We have in years past added liquid dehydrators to the condensing units and/or compressors and we have some large manufacturers at this time who add small amounts of pure anhydrous methyl alcohol to the systems and our experience has been quite satisfactory providing the alcohol is used to take care of an

extremely small amount of moisture. We have, of course, encountered corrosion in large amounts where large quantities of alcohol was added to act as an anti-freeze in a system containing very large amounts of moisture. Just what these limits are I cannot say, but we consider the use of an anti-freeze an easy way of covering up for poor workmanship, improper dehydration, etc. We believe the use of alcohol leads to sloppy workmanship because to a service man if one cc is good for a given amount of refrigerant four cc is four times as good. This leads to trouble."

-- Bendix Westinghouse --

"It has been our practice to void the warranty when this or other foreign substances are used in the refrigerating system. We have definitely found that methyl alcohol in our hermetic systems is injurious and have therefore ruled against it."

-- Frick Company --

"We have used Methyl Alcohol in varying quantities in field installed plants. We also have reports from many of our agents regarding the use of such material.

"The results of all such experiments have brought us to the conclusion that the use of Methyl Alcohol with any refrigerant is improper and should be avoided."

-- York Division --

"We have consistently recommended against the use of methyl alcohol in refrigerant systems and, consequently, we have no experience which we could offer to you in answer to your inquiry."

-- Tenney Engineering, Inc. --

"This is to advise that our company is under the impression that methyl alcohol is considered a contaminant at this time in a refrigerant system, and its use is frowned upon by hermetic compressor manufacturers.

"Our company does not employ methyl alcohol as an antifreeze. We utilize a process of gas charging and evacuation for dehydration of our refrigeration systems."

-- Carrier Corporation --

"We have no test data on the effect of methyl alcohol, however we are considerably influenced by the work done at duPont which shows that methyl alcohol under certain circumstances is harmful, and we are willing to accept their data."

-- Dr. W. O. Walker --

"Tests indicate that methyl alcohol in quantities less than 1% probably does not cause corrosion in Refrigerant 12 and possibly might not in 22 although there are no tests on the latter that I am acquainted with. If moisture is present, its effect will be additive to the alcohol."

Question 2

What is the moisture limit in R12 and R22 systems with regard to corrosion of iron, copper, and aluminum?

Very little factual information was obtained on this question.

The DuPont Company comments as follows:

"We do not believe that a permissible moisture limit in Refrigerant 12 and Refrigerant 22 systems with respect to corrosion of metals has been established. Laboratory sealed glass tube tests indicate that in the absence of motor insulation materials, the effect of small amounts (5 to 80 ppm) of moisture on refrigerant decomposition is negligible (Refrig. Eng. 65, 40, Nov. 1957). The quality of the oil is probably of more significance."

R. J. Thompson, Kinetics Chemicals Inc. reporting in Industrial and Engineering Chemistry Vol. 24, 1932, states that: Freon, saturated with water at 80F, when sealed in glass tubes with specimens of aluminum, brass, cast iron, copper, Dural metal, bronze, galvanized iron, Babbitt metal, lead, monel metal, magnesium alloy, silver, steel, tin solder, zinc, and Y metal for four months at 235F corroded only Y metal and magnesium alloy. Brass, copper, and lead were somewhat discolored, but not corroded. (Freon, saturated at 80F, contains about 98 ppm of water.)

Highside Chemicals Company reports in 1940 that a compressor valve plate in a Freon-12 system showed corrosion after eight months' operation with a water content of 300 ppm.

Ansul Chemical Company reported the following data in response to this question:

"This is a highly controversial subject. Our main emphasis has been in determining the corrosion limit for moisture in an open type F-12 operating system. Small quantities of moisture were added to this system and a specially designed filter block containing Whatman No. 1 filter paper was installed in the liquid

line. Whenever a moisture concentration of 15 ppm was reached corrosion solids collected on the filter paper within 24 hours. The above test does not indicate whether corrosion would occur with lesser amounts of water in Freon-12 over a prolonged period but does indicate that corrosion can occur within a very short period at 15 ppm water in Freon-12. This system contained copper and steel but no aluminum. This same test was repeated very recently and corrosion occurred at 16 ppm as analyzed by the Model W water analyzer.

"Our most recent experience with Freon-22 has been that corrosion solids collected on a filter in 24 hours when a moisture concentration of 135 ppm was reached. This, too, was an open type unit having a discharge pressure of 185 psig and 35 psig suction pressure and a liquid line temperature of 82°F. To our opinion this test is not conclusive since it is composed of only one run. Furthermore the test conditions to our opinion were very mild and corrosion solids could occur at a much lower moisture than 135 ppm."

Question 3

What is the moisture limit in R12 and R22 systems with regard to deterioration of the hermetic motor insulation?

Practically no data were obtained on this subject. Generally, manufacturers believed that it depended on the type of insulation and that the limit was higher than the limit for corrosion.

Question 4

If methyl alcohol were permitted in new systems, what should the limit be?

Nine manufacturers recommended that no methyl alcohol be permitted in refrigerating systems; five manufacturers stated that a limit of 1/2% by weight or less was an acceptable limit; and one person stated that 1% by weight was probably an acceptable limit.

Question 5

If methyl alcohol were permitted in new systems, how could the purchaser know that the initial dehydration of the system was thorough?

All but two manufacturers replied that the customer would not know what the initial water content of the system was. One manufacturer believed that the moisture content and alcohol content could be shown in the manufacturer's literature. Another manufacturer replied that the moisture in the refrigerant could be determined by the gravimetric method, the Karl Fischer method, or by DuPont's electrolytic water analyzer.

The DuPont Company commented as follows:

"The purchaser of refrigeration equipment has to depend on the integrity of the manufacturer as far as initial dehydration of the unit is concerned. Those manufacturers who use methanol provide the same warranties as those who do not. There are many problems connected with the analysis for water in assembled units including getting a representative sample and recharging the unit with new refrigerant (and oil) or returning the analyzed sample. Methanol will not interfere with the analysis for water by the Karl Fischer method. This method has been used for analyzing assembled units, but it is not as adaptable as the Electrolytic Analyzer or the Weaver conductivity method. Alcohol is known to interfere with these methods."

Question 6

Would methyl alcohol and R12 or R22 remain mixed in a refrigerant charging tank if mixtures were prepared in large quantities in a manufacturer's plant?

All respondents believed that mixtures of R12 or R22 with methyl alcohol would remain mixed in storage.

An analysis by the Quartermaster Research and Engineering Command indicates that the percent alcohol in the remaining refrigerant in a drum would gradually increase as increments of liquid were drawn off. The difference in vapor pressure of the two refrigerants and methyl alcohol would cause proportionately more refrigerant to be evaporated into the vapor space as the tank was emptied by repetitive withdrawals.

Question 7

Would the methyl alcohol and any water present in a system tend to accumulate in the evaporator, or would oil circulation tend to return it to the compressor?

Most respondents believed that the methyl alcohol and water would not tend to accumulate in the evaporator. There were two exceptions.

-- Kelvinator Division ---

"Some moisture, depending upon the concentration could accumulate as ice in the lowsides held at extremely low temperatures, while methanol will tend to circulate with the refrigerant along with that water held in solution by the circulating refrigerant at the prevailing temperature. The circulating oil in the system does not directly effect the distribution of methanol and/or moisture."

-- Frigidaire Division --

"In an operating system at proper charge moisture and alcohol will be circulated in similar manner to the oil. In a system shut down after running, the moisture and methanol can concentrate in the evaporator.

"Alcohol causes less damage while the equipment is running than it does in storage. The alcohol will tend to concentrate in the evaporator and during storage, when freon flow has practically ceased, pin-point corrosion is bound to exist at the point where the alcohol/water concentrates in the evaporator. This is a particular hazard with the new Roll-Bond aluminum evaporators. If the corrosion should not completely penetrate the wall, the wall is weakened; also the corrosion by-products are a serious hazard. He feels that this storage condition would be of particular concern in Army use since the refrigerators are run before acceptance, and then they are often put into storage for extended periods."

IV. LABORATORY STUDIES OF MISCIBILITY

Some limited studies were made at the National Bureau of Standards of the miscibility of R12, chemically pure methyl alcohol, water, and refrigerant grade oil. The mixtures were made in unsilvered Dewar flasks at atmospheric pressure so any separation of the liquids could be observed. Under these conditions the refrigerant gradually evaporated at a temperature of about -20F. The following results were observed:

1. Refrigerant 12 and methyl alcohol were miscible.
2. When 1/2% water and 1/2% methyl alcohol were added to R12 in that order, beads of ice were formed as the water was poured in and the ice beads were slowly dissolved after adding the alcohol with constant

stirring. Finally, the mixture of alcohol and water floated on the surface of the refrigerant in a broad, flattened puddle.

3. When the alcohol was added to the R12 first, small flaky ice crystals were formed temporarily on adding the water, and the mixture of alcohol and water floated on the surface of the refrigerant the same as before.
4. When 1/2% methyl alcohol and 0.1% water were added to R12 in that order the alcohol-water mixture floated on the surface as in the other tests. Increasing the amount of alcohol five-fold did not disperse the floating liquid, but appeared to spread it out. Increasing the ratio of alcohol to water to 50 to 1 by weight dispersed the floating liquid, leaving an apparent homogeneous mixture.
5. Methyl alcohol and refrigerant oil do not mix.
6. When 1/2% alcohol and 1/2% water were added to a half-and-half mixture of R12 and oil the mixture of alcohol and water floated on the surface of the oil-refrigerant mixture. Increasing the proportion of alcohol did not disperse the alcohol-water mixture into the refrigerant and oil.
7. A 60 to 40 ratio of water to methyl alcohol has a freezing temperature of about -20F. When such a mixture was added to R12 in an amount equivalent to 1/2% water to weight of R12, no ice was formed, but the mixture floated on top of the refrigerant. When increments of 1/4% of pure water by weight were added ice crystals were formed and later dissolved, but the floating liquid gradually took on a consistency like creamy, partly-crystallized honey. No hard ice crystal formation was evident until the water content was slightly in excess of 3 1/2% of the weight of refrigerant and about seven times the weight of alcohol.
8. When successive increments of this 60 to 40 mixture of water to methyl alcohol were added to R12 the floating material gradually took on this same creamy, partly-crystalline consistency observed when excess water was added.

V. NBS TESTS OF A WAREHOUSE UNIT CONTAINING METHYL ALCOHOL AND WATER

In August 1947 the National Bureau of Standards made tests of a one-ton warehouse unit to determine the effectiveness of methyl alcohol as an antifreeze when operating at -10F evaporator temperature. The system held about 25 lb of Freon-12 and was charged with 0.2% methyl alcohol. It was found that 0.8% water by weight could be added before any difficulties with freezing at the expansion valve occurred. After 30 hours' operation of the system considerable rust was found on the valves and valve plates. A water content of 0.8% corresponds to 8000 ppm and is well above the corrosion limit of iron in an R12 system.

VI. DISCUSSION AND CONCLUSIONS

The information obtained during this survey does not provide overwhelming evidence either for or against the use of small percentages of alcohol in domestic refrigerators.

Five out of six manufacturers of refrigerators who have experimented with the use of 1% or less of methyl alcohol in R-12 and R-22 systems indicate satisfactory performance providing the moisture in the system is kept at a very low level. Some of these manufacturers state that the discoloration and corrosion of metals is measurable but not objectionable under these conditions. Two of the six manufacturers now use 1/2% or less methyl alcohol regularly in their domestic refrigerators and one other uses small amounts in one of their home freezer models.

One large manufacturer of R-12 and R-22 refrigerants who has conducted sealed tube tests with mixtures of these refrigerants and 1% methyl alcohol states that the use of methyl alcohol by manufacturers in amounts of 1% or less of the weight of refrigerant is acceptable.

There is general agreement that the use of alcohol in larger amounts in R-12 or R-22 systems will cause excessive corrosion with or without the presence of water. There is general agreement that the initial moisture content of such systems should be kept at 25 ppm or lower regardless of whether methyl alcohol is used or not.

Data received from several manufacturers on their factory dehydration processes indicate that the principal difficulty is the moisture retained in motor windings and in the mechanical components of the system after assembly. Three manufacturers

quoted residual moisture contents ranging from 0.10 gram to 0.135 gram in their assembled systems after dehydration and before adding oil and refrigerant. No difficulty was cited in obtaining oil and refrigerant with 10 ppm of water or less in each. In a system with residual moisture in the range from 0.10 gram to 0.135 gram and charged with 6 lb of refrigerant and oil of 10 ppm moisture concentration, the total moisture would average 40 to 50 ppm concentration. A part of the residual moisture would remain in the motor windings under normal operating conditions, but if the operating conditions were such that the moisture in the windings were transferred to the refrigerant the moisture content of the circulating refrigerant could exceed 25 ppm.

The use of methyl alcohol makes the initial dehydration procedure less critical and potentially could permit poor quality control with regard to factory dehydration. It probably reduces the dehydration cost a little. Small percentages of methyl alcohol in a refrigerating system permit at least 1 1/2 times as much water as alcohol to be present in the system before freezing occurs at evaporator temperatures from -10F to -20F. This ratio may vary with the type of expansion device used. Thus 1 percent of methyl alcohol (equivalent to 10,000 ppm) in a system would permit a moisture concentration of 15,000 ppm before a freezeup would occur at -20F.

Laboratory tests show that, unless the percentage of alcohol exceeds the percentage of water by a ratio of more than 25 to 1, a mixture of alcohol and water will float on the refrigerant surface when the water content is 0.1% by weight of the refrigerant or more. Experiments with lower percentages of water were not made. Laboratory tests and some manufacturers' experience indicate that the alcohol-water mixture could accumulate in the evaporator on the surface of the refrigerant during storage conditions or when the unit was not running and might produce accelerated corrosion in that area.

Limited experimental data indicate that the moisture limit in R-12 and R-22 systems with regard to corrosion is probably in excess of 100 ppm of water, but less than 300 ppm without methyl alcohol being present. Thus in a system without an antifreeze, freezeup at the expansion device serves as a warning against conditions likely to produce corrosion. With as little as 0.2% methyl alcohol in a system the moisture content could exceed the corrosion limit many fold before a freezeup would furnish any warning of excessive moisture.

There is apparently no simple method by which the Federal government can test a production unit for moisture content as a part of its inspection procedures. Manufacturers state that the Karl Fischer method can be used for moisture analysis on a system containing alcohol, but it is not readily adapted to inspection

procedures. Both the DuPont electrolytic analyzer and the Weaver method are affected by the presence of alcohol. There are color-change moisture indicators appearing on the market at the present time, but their adequacy as inspection devices has not been evaluated by the National Bureau of Standards.

Neither the National Electrical Manufacturers Association nor the Air Conditioning and Refrigeration Institute has recognized the use of methyl alcohol in refrigerating systems as good practice nor has there been any standard adopted by these associations for the application of liquid antifreezes to refrigerating systems.

More technical data is needed on the effect of liquid antifreezes in refrigerating systems and on the corrosion limits of various materials of construction in the presence of moisture in such systems. Based on the data available it would appear that there might be a small margin of moisture content in R-12 and R-22 systems between the upper limit which will not cause freezing at the expansion device and the lower limit for corrosion. If small percentages of methyl alcohol have any place in such refrigerating systems it would be as an antifreeze within this range of moisture content. It should not be used in any system where normal operation or maintenance procedures could permit even small percentages of alcohol (less than 1%) to cover up or accommodate excessive amounts of moisture in the system.

The useful life of a thermally-sealed hermetic system depends almost entirely on whether or not the system remains leak-tight and on the initial condition created at the time of assembly insofar as the effects of moisture are concerned. This indicates that a low moisture limit should be specified for such systems whether or not alcohol is permitted. Assuming that the Federal government does not typically repair thermally-sealed hermetic systems when they fail, there is little opportunity to introduce excessive amounts of alcohol or moisture in these systems as a result of servicing and repair procedures.

This line of reasoning does not apply to mechanically-sealed hermetic or open type systems which by their design permit compressor repairs, leak repairs, and recharging by service groups. In such systems small amounts of methyl alcohol (less than 1%) could accidentally or deliberately be used to cover up or accommodate moisture in amounts that would produce corrosion.

Based on the information accumulated during this survey and on the above analysis our opinions are as follows:

1. All types and classes of domestic refrigerator systems should be dehydrated at the factory to a moisture content not to exceed 25 ppm.
2. Thermally-sealed hermetic systems in domestic refrigerators containing 1% or less of methyl alcohol in relation to the refrigerant charge when new should be considered acceptable.
3. The introduction of methyl alcohol in new mechanically-sealed or open type systems at the factory should be prohibited.
4. Investigations should be initiated immediately to find a suitable method for determining the alcohol and moisture contents of new domestic refrigerators as a part of the inspection procedure at the time of purchase.
5. Further research on the effects of moisture and antifreezes in refrigerating systems should be undertaken to provide a sound basis for specification requirements.



E. I. DU PONT DE NEMOURS & COMPANY

INCORPORATED

WILMINGTON 98, DELAWARE

ORGANIC CHEMICALS DEPARTMENT

FREON* PRODUCTS DIVISION

June 18, 1958

Ref. File No. 10.3

Mr. Paul R. Achenbach, Chief
Air Conditioning, Heating,
and Refrigeration Section
National Bureau of Standards
Washington 25, D. C.

Dear Mr. Achenbach:

This is in reply to your letters to R. C. McHarness and B. J. Eiseman of our "Freon" Products Division. We have prepared some comments on the use of methanol as an antifreeze in refrigerating systems using the "Freon" refrigerants. A copy is attached to this letter.

In answering your specific questions, we have the following additional comments.

1. We have no firsthand knowledge concerning the corrosive effect of one percent or less of methanol in "Freon-12" or "Freon-22" systems over a long period of time under typical operating conditions. Some manufacturers have reported good experience with its use (ASRE Meeting in Boston, 1956), but we know of no published data on unit tests. In limited laboratory sealed glass tube tests at 250°F for 115 days, one percent methanol had no significant effect on refrigerant decomposition (Refrig. Eng. 65, 40, Nov. 1957).
2. We do not believe that a permissible moisture limit in Refrigerant 12 and Refrigerant 22 systems with respect to corrosion of metals has been established. Laboratory sealed glass tube tests indicate that in the absence of motor insulation materials, the effect of small amounts (5 to 80 ppm) of moisture on refrigerant decomposition is negligible (Refrig. Eng. 65, 40, Nov. 1957). The quality of the oil is probably of more significance.
3. Little has been published on the effect of moisture on hermetic motor insulation. We would not expect a harmful effect on conventional insulation materials from small amounts of moisture.
4. If methanol is used as an antifreeze, it should be limited to one percent on the weight of the refrigerant. The purchaser of refrigeration equipment has to depend on the integrity of the manufacturer as far as initial dehydration of the unit is concerned. Those manufacturers who use methanol provide the same warranties as those who do not. There are many problems connected with the analysis for water in assembled units including getting a representative sample and recharging the unit with new refrigerant (and oil) or returning the analyzed

sample. Methanol will not interfere with the analysis for water by the Karl Fischer method. This method has been used for analyzing assembled units, but it is not as adaptable as the Electrolytic Analyzer or the Weaver conductivity method. Alcohol is known to interfere with these methods.

6. Methanol is miscible with liquid refrigerant and there would be no reason to expect separation in a charging tank.
7. Methyl alcohol, water or oil will not accumulate in a properly designed evaporator and suction line. Turbulence of the refrigerant liquid and velocity of the gas are usually sufficient to carry along other liquids that might be present.

A reprint of some of the work we have carried out at the "Freon" Products Laboratory bearing on the above questions is attached. It was published in REFRIGERATING ENGINEERING 65, 40, (1957). We hope the information will be of help to you in considering the advisability of using methanol as an antifreeze agent. If we can be of assistance to you on the application of our "Freon" refrigerants, please let us know.

Very truly yours,

"FREON" PRODUCTS DIVISION



D. E. Kvalnes
Manager
Technical and Sales Development

DEK/ba
Encl.

METHANOL IN REFRIGERATION SYSTEMS

Based on laboratory tests and industry experience, it appears that methanol in amounts of one percent or less based on refrigerant is acceptable in systems using "Freon-12" or "Freon-22" refrigerants. However, larger amounts, especially in systems containing aluminum, should not be used. The methanol problem lies with its uncontrolled use in field service.

Some manufacturers of refrigeration compressors regularly add methanol in amounts up to about one percent by weight based on the refrigerant. Experience with this procedure over a period of years has been good. Apparently, the use of methanol under these conditions with strict manufacturing control is not harmful. Units produced by these manufacturers are warranted for the same periods of time as others who do not use methanol. Limited laboratory tests tend to confirm the conclusion that small amounts are acceptable. In tests at 250°F for 115 days, the effect of one percent methanol was not significant (Refrig. Eng. 65, 40, Nov. 1957).

While methanol may be safely added to refrigeration equipment by manufacturers, its use is often abused under field service conditions. It may serve as a temporary expedient for the prevention of ice formation in capillary tubes or expansion valves but it can lead to serious trouble. We do not recommend the use of methanol under field service conditions for the following reasons.

1. It is generally better practice to remove the cause of trouble rather than to provide temporary relief by curing the symptoms. If excessive water is a current or potential problem in a system, effective and inexpensive driers are available for removing it. Current manufacturing procedures assure good dehydration, and good performance without alcohol has been well demonstrated.

2. Laboratory tests have shown that the presence of large amounts of methanol greatly increase refrigerant decomposition and metal corrosion in a relatively short period of time. Also, it is difficult in practice to resist the feeling that if a little is good more is better.
3. Addition of methanol does not remove water. Both the water and methanol remain in the system and over a period of time may chemically react not only with refrigerant, metals or oils but also with insulation materials or with foreign material that may have inadvertently entered the system.
4. Water and methanol (along with some air) contribute to the formation of metal oxides. Iron and copper oxide are catalysts for the decomposition of "Freon-12" and "Freon-22" (Refrig. Eng. 65, 33, Sept. 1957).
5. Many laboratory tests show that methanol can react with aluminum regardless of its effect on refrigerant or other metals present. This reaction produces a grey gelatinous mass and the presence of hydrogen has been demonstrated. In one test "Freon-12" containing four percent methanol with oil, aluminum, copper and steel was stored for 60 days at 250°F. At the end of the test a vapor sample contained over 50 percent hydrogen by volume. In similar tests containing two and four percent methanol with "Freon-12" and "Freon-22" there was a greater degree of copper plating and attack on the aluminum than in the control tests without methanol.

The reaction of aluminum with ethanol has also been demonstrated (Soap and Sanitary Chemicals, Vol. XXVI, No. C.S.M.A. (2), 1950).

PHILCO CORPORATION

REFRIGERATION & RANGE ENGINEERING DIVISION
TIOGA & C STREETS

PHILADELPHIA 34
PENNSYLVANIA

May 6, 1958

U. S. Department of Commerce
National Bureau of Standards
File Number 10.3
Washington 25, D. C.

Attention: Mr. Paul R. Achenbach, Chief,
Air Conditioning, Heating,
and Refrigeration Section

Dear Mr. Achenbach:

In reply to your inquiry of April 17 regarding "Methyl Alcohol in Refrigerants", please be advised that we feel that the questions you asked should be answered on an Industry basis. Accordingly, we are asking our Company Representative to bring this matter up with the proper Committees of both NEMA and ASRE.

Yours truly,

PHILCO CORPORATION

C. R. Quinn - Manager
Refrigerator & Freezer
Engineering

CRQ:bg

GENERAL  ELECTRIC
COMPANY

APPLIANCE AND TELEVISION RECEIVER DIVISION

APPLIANCE PARK . . . LOUISVILLE 1, KENTUCKY . . . TELEPHONE GLENDALE 4-7511

May 8, 1958

Mr. P. R. Achenbach, Chief
Air Conditioning, Heating,
and Refrigeration Section
National Bureau of Standards
Washington 25, D.C.

Re: File No. 10.3

Dear Mr. Achenbach:

I have made some inquiries regarding the questions contained in your letter of April 17, 1958. Unfortunately they lie for the most part outside our experience in the field of refrigeration for home use. The following summarizes findings corresponding to the questions which you enumerated:

1. The effect of methyl alcohol has not been investigated.
2. The presence of water results in capillary "freeze-up" at levels below that at which any corrosion problems appear with our present design.
3. The chief source of moisture is in cellulosic motor insulation and plastic wire insulation. With both R12 and R22 systems, our problem is to remove the water to prevent the failure noted above. A dryer is included in the system to maintain low moisture levels throughout service life.
4. We have no information as to a limit for methyl alcohol.
5. No help.
6. Methyl alcohol and freon mixed within miscibility limits for the temperatures involved would be stable.
7. We believe in our system that the mixture would circulate. This would depend on design.

We know of no policy for or against methyl alcohol for this use.

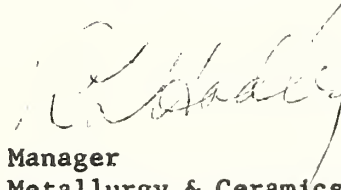
P. R. Achenback (con't)

-2-

A likely source for a great deal of this information is the duPont Company and their publication such as Kinetic Technical Bulletin B-5.

I hope this information proves to be of some value.

Very truly yours,



Manager
Metallurgy & Ceramics Laboratory
MAJOR APPLIANCE LABORATORIES

RL HADLEY:cc

DAVISON CHEMICAL COMPANY
DIVISION OF W. R. GRACE & CO.
BALTIMORE · 3 · MARYLAND

May 2, 1958

Mr. Paul R. Achenbach, Chief
Air Conditioning, Heating,
and Refrigeration Section
U. S. Department of Commerce
National Bureau of Standards
Washington 25, D.C.

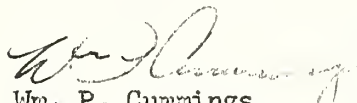
Dear Mr. Achenbach:

I am writing in reference to your letter of April 17th,
your File 10.3

Davison Chemical Company has conducted no research
relative to the corrosive nature of alcohol in refrigeration
systems. However, in view of the several published papers in
which it is indicated that this material is quite undesirable,
we do not recommend its use to any of our customers.

You indicated in your letter that you had access to
some of the information published by Ansul Chemical Company.
To our knowledge, they have probably published more data on
this subject than any other firm, and I am sure they will be
able to provide you with much information in addition to what
you obtained in their "News Notes."

Cordially yours,



Wm. P. Cummings
Technical Service Representative
Industrial Chemicals

WPC/vb

CARRIER CORPORATION

CARRIER PARKWAY, SYRACUSE 1, NEW YORK

April 28, 1958

Mr. Paul R. Achenbach
U. S. Department of Commerce
National Bureau of Standards
Washington 25, D. C.

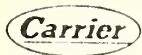
Dear Mr. Achenbach:

Subject: Methyl Alcohol in Refrigerants
Your File No. 10.3

This is in reply to your letter of April 17 regarding the practice of using methyl alcohol as an antifreeze agent in Refrigerant 12 and 22 systems.

I am sorry that we do not have data which relates to many of your questions, however we will try to do the best we can with the information we have available. Our comments to the questions you have listed are as follows:

1. We have no test data on the effect of methyl alcohol, however we are considerably influenced by the work done at duPont which shows that methyl alcohol under certain circumstances is harmful, and we are willing to accept their data.
2. This question, as far as I know, has not been specifically answered by our industry. We have ran extensive tests on the corrosion of metals in Refrigerants 11 and 113, arriving at the conclusion that water below saturation is not detrimental to metals in any way. We are inclined to believe that the same applies to Refrigerants 12 and 22. This fact seems to be borne out by the paper by Divers and Beacham which is attached, and which shows that the volume resistivity of saturated refrigerant is not affected by moisture up to 100% saturation.
3. The answer to this question depends to a certain extent on the insulation system considered. For example, a Lecton coated magnet wire-Mylar slot liner system is currently under consideration by Carrier, and I suppose by others in our industry. This system would be highly satisfactory in perfectly dry systems or in systems where the motor operating temperature is below 105°C and some moisture is present. In equipment operating above 105°C with moisture present, the Mylar slot liners would have to be coated to prevent deleterious hydrolysis reaction. In other words, various



Mr. Paul R. Achenbach

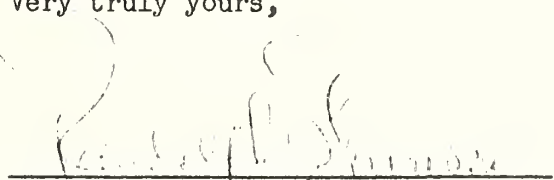
April 28, 1958

materials have different degrees of resistance to hydrolysis, and moisture level in the system would have to be adjusted to suit the materials used.

4. We would not tolerate the use of methyl alcohol in new systems, largely because we can see no reason why the original factory processing should leave residual moisture in an amount which would require its use.
5. We do not know. This would be a very difficult analytical job.
6. The best information we have on this is in duPont's Kinetic Technical Bulletin B-7 which indicates that methyl alcohol is quite soluble in R-12 and R-22.
7. We believe that the alcohol would not necessarily accumulate in the evaporator. We are not sure whether it would return to the compressor and stay there, however.

We have not done research work on methyl alcohol. We have a broad policy which recommends against its use for any purpose. We do find, however, that in isolated cases, some of our field people will resort to its use.

Very truly yours,



RANDOLPH STENERSON, Director
Materials and Processes Department
Research and Development Division

RS/lg
Att.

Whirlpool CORPORATION

EVANSVILLE DIVISION
EVANSVILLE, INDIANA

May 27, 1958

U. S. Department of Commerce
National Bureau of Standards
Washington 25, D. C.

Attention: Mr. Paul R. Achenbach, Chief,
Air Conditioning, Heating,
and Refrigeration Section

Dear Sir:

File 10.3

Item 1. We do not use methyl alcohol in our system as it serves us no purpose as we have no "freeze-ups."

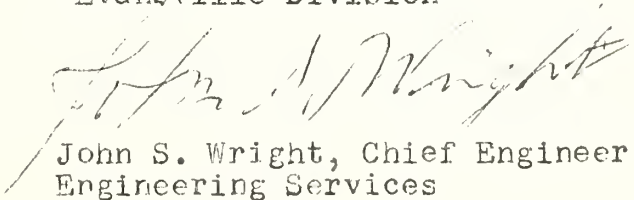
Item 2. and 3. We have found that by dehydrating to a limit of 0.1 gr. per assembly under 250°F. of heating and 200 micron or less pressure gives us a unit that when using F-22 is chemically stable and a unit plus dryer (silica gel) when using F-12 is stable.

Item 4, 5, 6, and 7. See Item 1.

We feel that alcohol serves no useful purpose and offers another element to the chemical stability problem and, therefore, should not be used.

Yours truly,

WHIRLPOOL CORPORATION
Evansville Division



John S. Wright, Chief Engineer
Engineering Services

JSW:jb

cc: Messrs. F. J. Hausfeld
E. T. Morton



HIGHSIDE CHEMICALS INCORPORATED

Manufacturing Chemists

PRescott 7-0626

10 COLFAX AVENUE, CLIFTON, N. J.

June 5, 1958

U. S. Dept. of Commerce
National Bureau of Standards
Washington 25, D. C.

REF: File #10.3

ATTN: Mr. Paul R. Achenbach, Chief,
Air Conditioning, Heating,
and Refrigeration Section.

Dear Sir:

This refers to your letter of April 17, addressed to our predecessor corporation, Stewart Industries, Inc., on the subject of methyl alcohol in refrigerants. You will note from the enclosed that we manufacture a liquid dehydrant containing a water destruction agent which actually destroys the moisture. Methyl alcohol alone is only an anti-freeze, which permits the water to remain in the system.

We have reviewed the laboratory files of our predecessor corporation in an attempt to answer your specific questions. Unfortunately, we are not able to find sufficient information to give a complete answer.

Regarding question one, the test data which we have been able to locate indicates that the use of methyl alcohol in quantities of 1% or less does cause some corrosion over long periods of time. We are unable to answer questions number two and three regarding the moisture limit in refrigeration systems, due to practical side of both the corrosion and insulation problems. In other words, any moisture will tend to corrode the system and will tend to damage the insulation, but the degree of this damage might or might not be serious enough to cause the system to stop. Any moisture can be considered harmful, and should be removed.



ANSUL *Chemical Company - Marinette, Wisconsin*

June 3, 1958

Mr. Paul R. Achenbach, Chief Air Conditioning
Heating and Refrigeration Section
National Bureau of Standards
Washington 25, D. C.

Dear Mr. Achenbach:

Your letter with regard to the use of methanol in refrigerating systems and moisture corrosion limits has been referred to me for reply. We will attempt to answer each question in order as listed.

1. Our investigations on the use of methanol were carried out in the 1940s and did not involve the use of operating equipment. The most recent information available to us is published by DuPont which shows that Freon-22 stored in sealed glass tubes containing 1% by weight methanol and in contact with copper, iron and refrigeration grade oil will show very little decomposition at temperatures of 250° and 300°F. In this regard your best source for information would be such manufacturers as General Electric, Westinghouse, Carrier or Techumseh.

We have always taken the stand that no methanol should be used since even anhydrous alcohol will introduce moisture into the system in which it is used. Furthermore methanol itself is quite a reactive compound and can readily react with the component parts of the system, especially in the case of aluminum in which case trimethyl aluminum can be formed. Again, if a drier or dehydrator is in use in the system, the desiccant can adsorb the methanol thereby reducing its capacity for water.

2. This is a highly controversial subject. Our main emphasis has been in determining the corrosion limit for moisture in an open type F-12 operating system. Small quantities of moisture were added to this system and a specially designed filter block containing Whatman No. 1 filter paper was installed in the liquid line. Whenever a moisture concentration of 15 ppm was reached corrosion solids collected on the filter paper within 24 hours. The above test does not indicate whether corrosion would occur with lesser amounts of water in Freon-12 over a prolonged period but does indicate that corrosion can occur within a very short period at 15 ppm water in Freon-12. This system contained copper.

and steel but no aluminum. This same test was repeated very recently and corrosion occurred at 16 ppm as analyzed by the Model W water analyzer.

Our most recent experience with Freon-22 has been that corrosion solids collected on a filter in 24 hours when a moisture concentration of 135 ppm was reached. This, too, was an open type unit having a discharge pressure of 185 psig and 35 psig suction pressure and a liquid line temperature of 82°F. To our opinion this test is not conclusive since it is composed of only one run. Furthermore the test conditions to our opinion were very mild and corrosion solids could occur at a much lower moisture than 135 ppm.

We have always maintained that all refrigeration systems be kept as dry as possible. This is especially true of Freon-22 upon which more rigorous operating conditions are imposed.

We specify that water content should be below 15 ppm in F-12 units and below 25 ppm in F-22 units.

3. We have no data on the effect of moisture on hermetic motor windings.
4. To our knowledge, if methanol is used in new systems the purchaser would have no means of knowing whether the initial dehydration is thorough. It should be pointed out, however, that most of the manufacturers are very thorough in this respect since they are obligated to stand behind their warranty which in some case run as high as 5 years.
5. We have no information with regard to mixing of methanol and refrigerants. Our only experience in this regard is that methanol is miscible with F-12 and F-22 in all proportions to temperatures of -90°F.
6. It is our opinion that if the saturation level is not reached the moisture will be the same throughout the system. We have determined the desiccant moisture equilibria of alumina in both Freon-12 and Freon-22. The desiccant is preloaded with water and placed in a cylinder which is charged with refrigerant. After several days the refrigerant is analyzed for moisture content. Results are plotted on an adsorption isotherm. We have also installed driers preload with water into operating systems and analyzed these systems for moisture. The results of the two types of tests agreed within the range of experimental error.

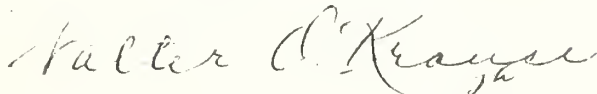
This would indicate that moisture does not accumulate in the evaporator.

Mr. Paul Achenbach
Page Three
June 3

We believe that W. R. Brisken of General Electric and
H. M. Elsey of Westinghouse have done some work in this re-
gard.

Yours very truly,

ANSUL CHEMICAL COMPANY

A handwritten signature in cursive script, reading "Walter O. Krause".

Walter O. Krause, Section Head
Refrigeration Applications Research

WOK:jmh



AMERICAN MOTORS CORPORATION

HUDSON AUTOMOBILES
SH AUTOMOBILES
ECIAL PRODUCTS

14250 PLYMOUTH ROAD
DETROIT 32 MICHIGAN

KELVINATO
AND LEONAR
APPLIANCE

May 13, 1958

U.S. Department of Commerce
National Bureau of Standards
Washington 25, D.C.

File No. 10.3
Subject: Methyl Alcohol in Refrigerants

Attention: Mr. Paul R. Achenbach, Chief
Air Conditioning, Heating,
and Refrigeration Section

Gentlemen:

Your questions relating to the above subject have been referred to the writer for comment.

We have been successfully employing methanol for over twenty years as an additive to refrigerant 12 for the purpose of preventing freez-up at the capillary inlet to the lowside. We have experienced no trouble relating to corrosion or compressor breakdown due to methanol, and our compressors and systems have been in continuous operation for the same length of time in the field.

1. Does methyl alcohol in quantities of 1% or less in refrigerant 12 or 22 systems cause corrosion either by itself or when combined with water over a long period of time under typical operating conditions?
 - A. We use less than 1% methanol in our refrigerant; actually, it is less than 0.5%. We have never found it necessary to use methanol in refrigerant 22 to prevent freez-up. At no time has corrosion been found to be a factor even under twenty years of typical operating conditions in the field.
2. What is the moisture limit in R12 systems with regard to corrosion of iron, copper, and aluminum?
 - A. According to extensive tests by du Pont as related in their technical bulletin #B-5 Table #II wet refrigerant 12 containing 98 ppm water does not attack iron, copper or aluminum. We do not feel that the moisture content of the circulating refrigerant in our systems should exceed 25 ppm run under specific conditions, which is far below the 98 ppm noted in du Pont's data.

Attn: Mr. Paul R. Achenbach

In Table VI of du Pont's report "Sealed Tube Tests with Hermetic System Components", stability of Al-Cu-Fe metals is similar to Cu-Fe at 250°F., and better at 300°F.

The specifying of a moisture limit in a R12 refrigeration system must at the same time specify the manner of sampling, details of system operation prior to sampling, basis of moisture calculation and method of moisture determination.

In our systems, we specify maximums of 0.135 g moisture for the total of mechanical parts, 10 ppm oil moisture and 10 ppm refrigerant. These values are sound practical manufacturing limits which are necessary to produce high quality products; they do not imply that the absolute moisture content is stable to these limits after the system is in operation due to cellulose water of hydration, nor do they imply that random checking of the oil or refrigerant will remain at these specified limits.

In the processing of a system, care must always be exercised to maintain the low moisture limit of the mechanical parts, for a proper evacuation of the system cannot be obtained if a "wet" system is produced. At present, we evacuate to a balanced pressure of 250 microns which would not be possible if our moisture content of the system was not within specifications.

As to corrosion of metals in a system of the qualities noted above, there is no danger under normal operating conditions. If operating conditions change to the extent of catalyzing chemical reactions or provoking material failure, moisture values will change as well as metal attack.

3. What is the moisture limit in R12 and R22 systems with regard to deterioration of the hermetic motor insulation?
- A. From our information, there is no harm to the motor insulation at the moisture limits which we specify.

Properly processed and cured wire film insulation such as Formex is impervious to moisture vapor as found in a hermetic compressor; and even during operation when submerged in oil having 70 ppm moisture content, no deterioration of the film has been observed by the writer. Both refrigerants 12 and 22 do penetrate the film to some extent with 22 having a definite deteriorating affect, but the refrigerant moisture content has not been considered by refrigerant or motor manufacturers to be a contributing factor; the writer concurs in this. It is the writer's belief that any limit of system moisture content which is set by specification to prevent oil or refrigerant breakdown and rust, would be sufficiently satisfactory for the wire film.

With regard to the other motor insulating materials such as cellulose and twine; these do have present, both, absorbed moisture

May 13, 1958

which is influenced by humidity, and water of hydration, which is part of the organic matter.

During compressor dehydration, the absorbed water of 2 to 3 grams is almost completely removed and in some cases, a small portion of the water of hydration is removed. Replacing this water does not impair the dielectric properties of the insulators. It has been found that during the compressor operation, system moisture will be absorbed from the freon and oil by this dry insulation during the "off" period, and released again during the "on" period. No harm to either the cellulose or twine insulation is expected from moisture present in the 12 or 22 systems which is within the specifications controlling corrosion or refrigerant and oil breakdown.

4. If the use of methyl alcohol were permitted in new systems, what should the limit be?
 - A. We specify 2 ml methanol per pound refrigerant 12 (0.35% by weight) which is sufficient methanol for our systems which have less than 0.135 g of water remaining after dehydration. du Pont have stated in their test results of "Sealed-Tube Tests with Hermetic System Components" that "the effect on F-12 decomposition of 1% of methanol (on the weight of the refrigerant) was determined to be insignificant in copper and mild steel systems (Table VI)".
5. If methyl alcohol were permitted in new systems, how could the purchaser know that the initial dehydration of the system was thorough?
 - A. Moisture in oil can be titrated by the Karl Fisher method.

Moisture in refrigerant can be determined by gravimetric check; titrated by a modified Karl Fisher method, or measured by du Pont's Electrolytic Water Analyzer. If the moisture in these components is below 25 ppm when operated and sampled to specific specifications, the system can be considered to have been properly dehydrated by the manufacturer. Methanol does not interfere in these last two methods. Here again, the migration of moisture and its amount at some point in a system is a variable depending upon operating conditions and charges, among others. The sampling of a system under a specific operating condition will furnish an empirical value of moisture present at the point of sampling which may not have any bearing on the total moisture of the system. Even with driers present in the system, their capacities may be exceeded at some time due to operating conditions and the system fail due to inadequate protection. The use of methanol on the other hand will furnish continued protection from freez-up under all conditions of operation due to its migration with the refrigerant.

6. Would methyl alcohol and R12 or R22 remain mixed in a refrigerant charging tank if mixtures were prepared in large quantities in a manufacturer's plant?

File No. 10.3
Attn: Mr. Paul R. Achenbach

-4-

May 13, 1958

- A. We have always mixed methanol with the refrigerant and have never found separation to exist.

We have always added methanol to the ton drum of refrigerant 12. As the result is a homogeneous solution of methanol in refrigerant, there is no separation. The exact amount of methanol is added under pressure and the drum either rocked for four (4) hours, or allowed to stand for 72 hours; either method will insure complete homogeneous mixing of the methanol throughout the refrigerant.

7. Would the methyl alcohol and any water present in a system tend to accumulate in the evaporator, or would the oil circulation tend to return it to the compressor?

- A. Some moisture, depending upon the concentration could accumulate as ice in the lowsides held at extremely low temperatures, while methanol will tend to circulate with the refrigerant along with that water held in solution by the circulating refrigerant at the prevailing temperature. The circulating oil in the system does not directly effect the distribution of methanol and/or moisture.

- Q. Has your company done research on the corrosive effects of methyl alcohol in refrigerating systems? Does your company have an opinion or a policy for or against the use of methyl alcohol in new hermetic refrigerating systems for operation at evaporator temperatures of zero F?

- A. Our company has determined by laboratory tests on compressors and systems made to our specifications that no corrosive effects of methanol result in typical operating conditions. We strongly support the use of methanol as an antifreeze in hermetic systems for operation in household or commercial application. Our present practice follows our contention and our field record supports our judgment that methanol does not create corrosive conditions.

It is hoped that the foregoing discussion has made our thinking clear and has relieved any doubts in your mind as to the advisability of permitting the use of methanol as an antifreeze in hermetic refrigerating systems under the conditions described.

Very truly yours,

AMERICAN MOTORS CORPORATION
Kelvinator Division

George T. Bauer

George T. Bauer
Assistant Chief Engineer

FREON, A REFRIGERANT

R. J. Thompson, Kinetic Chemicals, Inc., Wilmington, Del.

Corrosive Action

Test specimens of aluminum, brass, cast iron, copper, Dural metal, bronze, galvanized iron, Babbitt metal, lead, monel metal, magnesium alloy, silver, steel, tin solder, zinc, and Y metal, after being sealed in glass tubes with Freon under its own vapor pressure for 5 months at a temperature of 235°F.(112.8°C.), showed no visible evidences of corrosion except for a slight darkening of the surfaces of the aluminum, brass, copper, bronze, lead, and zinc. There was no perceptible pitting of the surfaces of any of the specimens.

Freon, saturated with water at 80°F.(112.8°C.) for 4 months with the above metals, corroded only Y metal and magnesium alloy. Brass, copper, and lead were somewhat discolored but not corroded.

In refrigerating equipment there may be present a small amount of free water, but there will never be a sufficiently high temperature under normal operating conditions (109.5°F., or 43°C. compression temperature--standard ton conditions) to cause corrosion of any of the metals used in compressor construction. Freon is only slightly soluble in water, and the solution formed will not corrode any of the common metals used in refrigeration construction.

CHEMICAL EFFECTS IN REFRIGERATING SYSTEMS

By E. W. McGovern
E. I. duPont de Nemours & Co., Inc.

Antifreezes, such as methyl alcohol, act merely as antifreezes--they do not prevent other moisture effects, such as corrosion. As a matter of fact, methyl alcohol itself, when mixed with a dry halogenated hydrocarbon refrigerant, produces a slightly corrosive mixture. If an antifreeze is used to open a frozen system, it should be followed by a chemical dryer.

A liquid moisture scavenger differs from an antifreeze in that it chemically reacts with water to form another compound. The scavenger itself, in the quantity used, and the water reaction products should be harmless to the refrigerating system. One such liquid drying agent is reported as giving good results when used in small amounts to take care of small amounts of water, but as being unsuitable for removal of large quantities of water.

Excerpt from article appearing in Refrigerating Engineering, May, 1942.

Westinghouse

ELECTRIC CORPORATION



ELECTRIC APPLIANCE DIVISION

PHONE BROADWAY 9-7311
300 PHILLIPPI ROAD
BOX 2199, COLUMBUS 16, OHIO

June 4, 1958

Mr. Paul R. Achenbach, Chief,
Air Conditioning, Heating, and Refrig. Section
U. S. Department of Commerce
National Bureau of Standards
Washington 25, D. C.

Subject: File No. 10.3
Methyl Alcohol in Refrigerants

Dear Mr. Achenbach:

Your letter of April 17 has been referred to me for reply.

I would like to point out at the beginning that the answers which you receive to your letter will contain more opinions than facts. Just as methods of manufacture vary from one manufacturer to another so do the processing specifications. This does not mean that one method is right and another is wrong, but does indicate that, with the many differences in detail design and application of a refrigerating system, there is more than one way to accomplish a satisfactory long life. If a manufacturer has had satisfactory service experience with a specific method of processing, he is reluctant to change his methods even if another method appears to be equally good.

Westinghouse does not use any type of anti-freeze in refrigerator compressors. We have run laboratory tests using methyl alcohol and have entered into discussions and compared test results with others on many occasions. The answers to your questions, however, are based on experience with these tests and are not the result of long-term field experience. |

With this background statement and explanation, I will attempt to answer your specific questions as follows:

1. I do not think that methyl alcohol in quantities of one per cent or less in refrigerant 12 systems will cause corrosion either by itself or when combined with water over a five or ten year period of time under typical operating conditions. This refers to one per cent by weight of the refrigerant. We have had no experience with alcohol in refrigerant 22 systems.
2. In household refrigerators and freezers the amount of moisture which can be tolerated is governed by the tendency to freeze up at the

YOU CAN BE SURE... IF IT'S Westinghouse

June 4, 1958

expansion end of the capillary tube rather than by corrosion. As insurance against freeze up, we dehydrate to a point where there is less than one hundred mg. of moisture left in the compressor, and then place a desiccant in the system to scavenge any moisture which might enter during assembly.

3. Here again the moisture limit is determined by the tendency to freeze up rather than by damage to the motor insulation.
4. It has been fairly well established that one half per cent methanol in systems has not been harmful.
5. The purchaser would have to rely entirely upon the reputation of the manufacturer that dehydration of the system had been thorough.
6. It has been my finding that methanol added to large quantities of refrigerant 12 in the amount of one half per cent, and thoroughly mixed, will enter the system as a true solution. We have had no experience with refrigerant 22.
7. I would not expect any problem with the methyl alcohol and water solution accumulating in the evaporator.

For further information of a more specific nature you may want to contact one of the following persons:

Dr. D. E. Kvalnes
Freon Products Division
E. I. du Pont de Nemours and Co., Inc.
Wilmington, Delaware

Dr. H. M. Parmelee
Freon Products Division
E. I. du Pont de Nemours and Co., Inc.
Wilmington, Delaware

Dr. W. A. Knapp, Research Consultant
General Chemical Division
Research Laboratory
P. O. Box 405
Morristown, New Jersey

Very truly yours,



James B. Kelley
Advanced Engineering Section
Refrig-Freezer Engrg. Dept.

/m

cc: Columbus Works - Mr. A. J. Pfeiffer, Mgr. Refrig-Freezer Engrg.
Mr. R. D. Smith, Secretary, Household Refrig-Freezer Section
National Electrical and Manufacturers Association, 155 E. 44th Street
New York 17, N. Y.

SUBSIDIARY OF

Admiral CORPORATION

May 21, 1958

Mr. Paul R. Achenback, Chief,
Air Conditioning, Heating & Refrigeration Section,
U. S. Dept. of Commerce,
National Bureau of Standards,
Washington 25, D.C.

Dear Mr. Achenback:

Your letter of April 17, 1958 with reference to the usage of Methyl Alcohol in refrigerants has been referred to the writer for reply. As you are probably aware the corrosive effect of alcohol in a refrigeration system has been discussed pro and con for many years in the refrigeration industry, and I am sure the views expressed here will not be in agreement with many of the experts from other manufacturers.

The answers are listed in the same sequence as the questions in your inquiry, and are based on experience with F-12 systems.

1. Results from extended life tests on units having one percent of alcohol indicate that the amount of corrosion on components is dependent to a great extent on the operating pressures and temperatures. Extensive copper plating was deposited on bearing surfaces in approximately six months on those units operating under accelerated test conditions of 235# head pressure and 250° motor winding temperatures. Similar units having a small fan in the circuit to maintain compressor housing temperatures below 150°F were comparatively free of plating after 12 months operation. The terminology "typical operating conditions" will vary with the unit designs of the individual manufacturer and it is the writer's opinion that the phrase should be more specific so there would be a common basis for comparison.
2. With reference to the minimum amount of moisture in a system that may result in corrosion of iron, copper or aluminum components in the compressor the manufacturers usually have definite ideas as to the allowable moisture content permitted based on past experience in the field.

2 - Mr. Paul R. Achenback

Admiral specifications permit a maximum moisture content of 10 P.P.M. in a system employing a dessicant, and to date this has proven satisfactory. However, it should be noted that the moisture limits are usually below 5 P.P.M. in the hourly checks of systems on the production line.

3. The rate of deterioration of motor insulation in the presence of moisture depends greatly on the operating temperatures of the windings during unit operation. It is an accepted fact that moisture migrates between the liquid and vapor phases of the refrigerants as well as between the refrigerant and motor insulation.

The compressors as received from the manufacturer are dehydrated and contain less than 0.10 gm moisture. Upon completion of final processing in our plant the moisture content is further reduced.

4. If Methyl alcohol were permitted in new systems it is recommended that the amount be not more than 1/2 percent of the refrigerant and oil charge.
5. To the best of my knowledge the consumer would have no idea as to the degree of dehydration the system has been subjected by the manufacturer as long as the unit functions properly.
6. To the best of our knowledge F-12 and Methyl alcohol will remain mixed in large quantities, but suggest you contact Gibson or Kelvinator as they have had several years experience in this process.
7. Inasmuch as the refrigerant, oil and alcohol are miscible there is little possibility that the alcohol would accumulate in the evaporator.

At the present time Admiral does not use alcohol in refrigeration systems since we use Tecumseh compressors and addition of alcohol to a system automatically voids the Tecumseh warranty.

Hoping this information may be of some value, we remain

Sincerely yours,

MIDWEST MFG. CORPORATION



W. F. Helsel
Chief Engineer - Applications

HOTPOINT COMPANY
5600 West Taylor Street
Chicago 44, Illinois

April 29, 1958

Mr. Paul R. Achenbach, Chief,
Air Conditioning, Heating, & Refrig. Section
U. S. Department of Commerce
National Bureau of Standards
Washington 25, D. C.

Re: File No. 10.3
SUBJECT: Methyl Alcohol in Refrigerants

Dear Mr. Achenbach:

Your letter of April 17th has been referred to the writer for an answer. You state you have been asked to "survey expert opinion" relative to this subject. We would like to suggest that you contact three other men in our industry who I am sure will give you the results of years of experience:

- (1) Dr. Howard M. Elsey, Chemical Consultant, 212 - Fifth Street, Oakmont, Pennsylvania. Dr. Elsey, now retired, was chief research chemist for Westinghouse and did a great deal of work with refrigerants and oils.
- (2) Dr. George Bauer is chief chemist for Kelvinator Division of American Motors Corp., 14250 Plymouth Road, Detroit 32, Michigan.
- (3) Dr. Ross, Sun Oil Co., 1608 Walnut St., Philadelphia 3, Penn.

Kelvinator, as you may or may not know, has been using alcohol in their household, F-12 systems for a great number of years. I am sure that Dr. Bauer will have information which will be of interest to you.

The answers given herein will be based on experience with only one refrigerant; namely, R-12 or F-12 as you choose. Answers are given under the same numbers as your questions.

1. Extended life tests (Hotpoint units with Kelvinator Compressors) on operating systems with less than 1% alcohol have shown no signs of corrosion. These tests included units with greater than 1% alcohol and to date, they have not shown any evidence of corrosion. These tests are still in progress. These tests included units with normal and excessive quantities of moisture also.
2. It is doubtful whether you will get an answer to this question. Any moisture beyond the limits now imposed by the Engineering Departments of the manufacturers is based upon the amount of moisture permissible without causing a "freeze-up" of the system while operating. Therefore, the limits are based on the projected amount of this residual moisture in the system before it is charged with refrigerant and the amount of money each manufacturer cares to invest in a desiccant which is inserted to "mop up" this residual moisture and preventing it from causing a "freeze-up".

TO: Mr. Paul R. Achenbach

4/29/53

R-12 as it is sold to the industry has a maximum moisture limit of ten parts per million. As it is delivered to the customer, their product usually runs five to seven parts per million. With the addition of the residual moisture in the refrigerating units as they are charged, most manufacturers set a total moisture limit for their systems as sold at less than twenty-five parts per million.

3. The possible deterioration of hermetic motor insulation is closely connected with the heat this insulation is subjected to during the cycling of the mechanical unit. As the stators, which contain hygroscopic material such as paper and cotton are delivered to the manufacturer, they have approximately $2\frac{1}{2}$ to $3\frac{1}{2}$ grams of water. Good processing by the unit manufacturer will bring this residual moisture down to approximately 0.10 grams. Should the cycling of the units after charging, release this residual moisture (due to operating temperature), it is possible to shorten the life of the motor due to breakdown of the hygroscopic materials mentioned.
4. It would be our suggestion that the amount of alcohol used should be held to less than 1/2% based on the total charge (by volume). All Hotpoint refrigerators for the past two years have been charged with R-12 with less than 1/2% alcohol. Field Service indicate no difficulty from "freeze-ups" and there have been no failures of motors attributable to alcohol addition or residual moisture.

In asking your question concerning the 1% of alcohol, you did not state whether you were thinking of this as 1% of total charge (oil and refrigerant) or 1% of oil or refrigerant charge only. You can readily understand that based on the amount of oil and/or refrigerant used in some systems, the basis for the 1% might make quite a difference. If it is your ultimate plan to establish a standard, it should be clearly stated on what the 1% is based; namely, total charge, oil or refrigerant separately.

In our case here at Hotpoint, we have several different charges of both oil and refrigerant. Given below, we have taken the maximum and minimum charge, percenting the alcohol used all three ways to give you some idea of the possible variation percentage-wise.

| | <u>OIL</u> | <u>R-12</u> | <u>BOTH</u> |
|-----------|------------|-------------|-------------|
| Maximum % | 0.13 | 0.10 | 0.15 |
| Minimum % | 0.09 | 0.03 | 0.06 |

5. Your question is not quite clear. If your interpretation of "purchaser" means the ultimate customer (the housewife), then we can say there is no manufacturer at present using alcohol who designates on the unit in anyway the thoroughness of the unit dehydration prior to refrigerant charging.
6. We believe the answer would be that the alcohol does remain mixed if applied to large quantities of freon before charging. We strongly recommend that you get a more complete answer from Mr. Lauer at Kelvinator since this company has used this method for adding alcohol for a number of years.

For your information, we here at Hotpoint add the alcohol at the charging board, automatically, with each measured charge of refrigerant, as it is delivered directly to the unit. A very accurate dispensing device adds 1.5 cc of alcohol to each refrigerant charge.

TO: Mr. Paul R. Achenbach

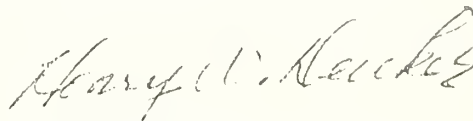
4/29/55

7. Since the alcohol, refrigerant and oil are miscible, there would be no accumulation of either of these separately. This may depend somewhat on the type of system, whether it is a "high pressure" or "low pressure" crankcase.

With reference to your last two questions (not numbered), I believe your first question is answered in my number one of this letter, and my statement verifying that we have used alcohol for the past two years, answers your second question.

In conclusion, we would be interested to know the reason for the survey you are making. If there is some thought of establishing a standard for permissible methyl alcohol additions, we would like to know the comments from the Engineering Departments of all the other manufacturers. Since all have representatives as members of our National Society ASRE, and since this Society has active committees for formulating standards for our industry, we strongly recommend that you contact Mr. Frederick J. Reed, Engineering Professor, Duke University, College of Engineering, Durham, North Carolina, who is at present the chairman of the ASRE Standards Committee.

Yours very truly,



Henry W. Deuker - Manager
Materials & Processes
Refrigeration Engineering
HOTPOINT COMPANY

HWD:pl



Copeland Refrigeration Corporation

Sidney, Ohio

May 6, 1958

Mr. Paul R. Achenbach, Chief
Air Conditioning, Heating,
and Refrigeration Section
U.S. Department of Commerce
National Bureau of Standards
Washington 25, D.C.

Subject: Methyl Alcohol in Refrigerants

Dear Mr. Achenbach:

We know of no conclusive data which will answer the questions listed in your letter of April 17. We have, however, had considerable experience in the use of Methyl alcohol in hermetic compressors over the past fifteen years.

We recommend that nothing be put into a hermetic refrigeration system except pure refrigerant, refrigerating oil and a suitable dehydrating agent - such as activated aluminum, Silica Gel, Molecular Sieve, etc., (no liquid dehydrants.)

We have in years past added liquid dehydrators to the condensing units and/or compressors and we have some large manufacturers at this time who add small amounts of pure anhydrous methyl alcohol to the systems and our experience has been quite satisfactory providing the alcohol is used to take care of an extremely small amount of moisture. We have, of course, encountered corrosion in large amounts where large quantities of alcohol was added to act as an anti-freeze in a system containing very large amounts of moisture. Just what these limits are I cannot say, but we consider the use of an anti-freeze an easy way of covering up for poor workmanship, improper dehydration, etc. We believe the use of alcohol leads to sloppy workmanship because to a service man if one cc is good for a given amount of refrigerant four cc is four times as good. This leads to trouble.

Yours very truly,

COPELAND REFRIGERATION CORPORATION

Ray Hoxley
Ray Hoxley
Chief Application Engineer

RM:ss

Bendix-Westinghouse

AUTOMOTIVE AIR BRAKE COMPANY

EVANSVILLE DIVISION

950 EAST VIRGINIA STREET
EVANSVILLE 11, INDIANA

April 25, 1958

Mr. Paul R. Achenbach, Chief,
Air Conditioning, Heating,
and Refrigeration Section
U. S. Department of Commerce
National Bureau of Standards
Washington 25, D. C.

Dear Mr. Achenbach:

In reply to your letter of April 17 on the subject of methyl alcohol in refrigerants, it has been our practice to void the warranty when this or other foreign substances are used in the refrigerating system. We have definitely found that methyl alcohol in our hermetic systems is injurious and have therefore ruled against it.

However, I think it would be well if you got the specific answers to your questions from DuPont who have gone into this matter much more thoroughly than we have; in fact, we have followed their recommendations in ruling against it.

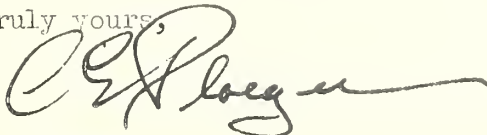
I would suggest that you write to:

Mr. R. C. McHarness
E. I. DuPont de Nemours & Company
"Freon" Prod. Laboratory
Chestnut Run
Wilmington 98, Delaware

or

Dr. B. J. Eiseman
E. I. DuPont de Nemours & Company
"Kinetic" Chemicals Division
Wilmington 98, Delaware

Very truly yours,

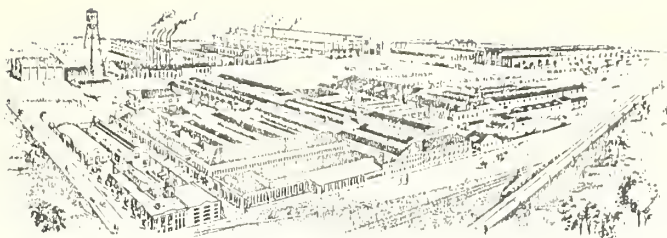


C. L. Ploeger
Director of Engineering

CMP:js

SUBJECT TO APPROVAL BY AN EXECUTIVE OFFICER OF THE COMPANY AT WAYNESBORO, PENNSYLVANIA.

EDICT, PRESIDENT
AUBREY, V. P. & ASST. GEN. MGR.
ROSCHLI, SEC. & TREASURER
DETWILER, ASST. SECRETARY



AIR CONDITIONING, REFRIGERATING
ICE MAKING & QUICK FREEZING EQUIPMENT
POWER FARMING MACHINERY
PORTABLE SAWMILLS

ADDRESS ALL
COMMUNICATIONS TO
THE COMPANY

FRICK COMPANY

ESTABLISHED 1853

TELEPHONE 1245
CABLE ADDRESS
FRICK (WAYNESBORO, PENNA.)

WAYNESBORO, PENNA., U.S.A.

May 21, 1958
"Wednesday"

U. S. Department of Commerce
National Bureau of Standards
Washington 25, D. C.

Attention: Mr. Paul R. Achenback, Chief,
Air Conditioning, Heating, and
Refrigeration Section

Subject: Methyl Alcohol in Refrigerants

Gentlemen:

This will acknowledge receipt of your letter of April 17th reference the above subject and we can reply to same in a general manner only.

We have never attempted the use of Methyl Alcohol in any factory assembled units.

We have used Methyl Alcohol in varying quantities in field installed plants. We also have reports from many of our agents regarding the use of such material.

The results of all such experiments have brought us to the conclusion that the use of Methyl Alcohol with any refrigerant is improper and should be avoided.

Where moisture was present in a system we did not secure freedom from freezing troubles at expansion valves until the quantity of Methyl added was increased to a point where it seriously and adversely affected evaporating temperatures.

Where a system had contamination such as, small copper cuttings we seemed to experience more copper plating and oil sludging when Methyl Alcohol was added to the refrigerant.

We have never attempted any precise measurement of moisture percentage.



In our overall experience we have found no substitute for a clean system wherein moisture has been eliminated by the proper initial evacuation or the inclusion of a proper dryer in the liquid supply line.

Field installations subject to maximum moisture contamination because of open lines during erection are made trouble free by the careful use of a liquid line dryer which is kept in service only for that length of time necessary to dry the refrigerant and then bypass.

We consider the continued flow of refrigerant through a desiccant dryer is improper.

While the above does not answer your questions in chronological order, we trust that it will give you our general experience in this matter.

Very truly yours,

FRICK COMPANY

BY *M. W. Garland*
M. W. Garland, Chief Engineer
Air Cond. & Refg. Mchy. Div.

MWG:BJSP

YORK

DIVISION OF BORG-WARNER CORPORATION
YORK, PENNSYLVANIA

May 13, 1958

Mr. Paul R. Achenbach, Chief,
Air Conditioning, Heating,
and Refrigeration Section
National Bureau of Standards
Washington 25, D. C.

Subject: Methyl Alcohol in Refrigerants.

Dear Mr. Achenbach:

This is in reply to your letter of April 17.

We have consistently recommended against the use of methyl alcohol in refrigerant systems and, consequently, we have no experience which we could offer to you in answer to your inquiry.

We would suggest that you contact Kinetic Chemicals Division of E. I. du Pont de Nemours & Co. We feel sure that they can supply you with considerable of the information which you are seeking.

Yours very truly,



R. F. Lauer
Vice President

RFL:M



Tenney

ENGINEERING, INC.

ENGINEERS AND MANUFACTURERS OF
REFRIGERATION AND ENVIRONMENTAL EQUIPMENT

PRINCIPAL OFFICES AND PLANTS
1090 SPRINGFIELD ROAD 2235 SISSON ST.
UNION, NEW JERSEY BALTIMORE 11, MARYLAND
MURDOCK 6-7870 TELEPHONES
NEW YORK BELMONT 5-5522
WORTH 2-0332
TELETYPE
UNVL 433 BA 168

Union, New Jersey
April 28, 1958

U. S. Department of Commerce
National Bureau of Standards
Washington 25, D. C.

Reference: Methyl Alcohol in Refrigerants

Attention: Paul R. Achenbach
Chief, Air Conditioning, Heating, and Refrigeration Section

Gentlemen:

With reference to your letter of April 17, 1958, this is to advise that our company is under the impression that methyl alcohol is considered a contaminant at this time in a refrigerant system, and its use is frowned upon by hermetic compressor manufacturers.

Our company does not employ methyl alcohol as an antifreeze. We utilize a process of gas charging and evacuation for dehydration of our refrigeration systems.

I am enclosing a copy of a letter from the American Society of Refrigerating Engineers describing a task force group studying the problem of contaminants. I feel sure that they would cooperate with you in supplying available information on the questions which you have put forth. Another source of information would be the Freon Refrigerant Group of the Du Pont Company, which has conducted extensive studies in this area.

Very truly yours,

TENNEY ENGINEERING, INC.

Bernard Friedman
Bernard Friedman
Technical Director

BF:JS
Enclosure - 1

CORAL GABLES 46, FLORIDA

May 6, 1958

OFFICE OF THE DEAN

DIVISION OF RESEARCH AND INDUSTRY

File No. 10.3

Mr. Paul R. Achenbach, Chief
Air Conditioning, Heating,
and Refrigeration Section
National Bureau of Standards
Washington 25, D. C.

Dear Mr. Achenbach; Subject: Methyl Alcohol in Refrigerants

I have your letter of April 23rd relative to the subject. At the outset, I can tell you that very little is known relative to the questions propounded in your letter. Where anything is known, the information is quite general.

Following is a quick run down on each of the questions contained in your letter.

1. Tests indicate that methyl alcohol in quantities less than 1% probably does not cause corrosion in Refrigerant 12 and possibly might not in 22 although there are no tests on the latter that I am acquainted with. If moisture is present, its effect will be additive to the alcohol.
2. Not known.
3. Not known.
4. Probably 1% by volume.
5. Not known.
6. Methyl alcohol will remain mixed with Refrigerant 12 indefinitely unless there is a distillation operation in which case it might or might not behave like water. At room temperature, certain Refrigerant 22 and methyl alcohol would remain mixed. I do not know whether they would separate into two saturated layers at lower temperatures. Nothing is known about the distillation characteristics of this mixture.
7. See remarks under No. 6.

UNIVERSITY OF MIAMI
CORAL GABLES 46, FLORIDA

OFFICE OF THE DEAN
DIVISION OF RESEARCH AND INDUSTRY

Mr. Paul R. Achenbach, Chief, - 2.


May 6, 1958

I cannot refer you to publications on any of these questions since, as far as I know, there is nothing covering the field. It seems that a large amount of research would need to be done in this area. Perhaps your government agency could finance such research.

I hope this information is of some value to you.

Kindest personal regards.

Very truly yours,



Walter O. Walker,
Dean.

W/m



Frigidaire

May 9, 1958

U. S. Department of Commerce
National Bureau of Standards
Air Conditioning, Heating and Refrigeration Section
Washington 25, D.C.

Attention: Mr. Paul R. Achenbach, File No. 10.3

Dear Sir:

The following are our comments in answer to the questions which you raise in your letter of April 17, 1958. We regret that in all too many cases the answers cannot be absolute or precise but must be estimates and opinion extrapolated from the data and experience at hand.

1. Methyl alcohol in quantities of 1% or less in R-12 or R-22 systems over long periods of time can cause visible corrosion and staining and iron and copper compound formation. If similar systems are test-run side by side, one dry and one with 1/2 to 1% methanol, the alcohol system can always be picked out as having more stain, corrosion, copper plating, and debris on fine filter screens than the dry system. However, for proper perspective, it does not necessarily follow that alcohol may never be used. There have been and are many instances of practical use of alcohol.
2. Although we presently operate below 25 ppm moisture in R-12 systems yet there are many thousands of systems that were operated satisfactorily at the 25 ppm level or even a bit higher. In R-22 systems in air conditioning units, the refrigerant may on occasion reach as much as 200 ppm H_2O , though generally 60 to 100 ppm is the practical level. Certain amounts of staining and corrosion can be observed particularly in condensers but this has had no significant effect on operation or life.
3. We make no distinction between allowable moisture levels for hermetic motor insulation deterioration and allowable levels for the rest of the system.
4. Where the use of methyl alcohol can be demonstrated to be safe and practical a level of 1/2% by wt. of the refrigerant charge should be adequate for household refrigerators. For other types of systems the design and operating conditions may require a higher level.

5. If methyl alcohol is present in a new system, there is no way of knowing whether initial dehydration was thorough except by analyzing the total refrigerant charge for moisture and alcohol and the compressor stator for free moisture.
6. Anhydrous methyl alcohol makes a true solution with dry R-12 or R-22 and would remain mixed in large charging tanks.
7. In an operating system at proper charge moisture and alcohol will be circulated in similar manner to the oil. In a system shut down after running, the moisture and methanol can concentrate in the evaporator.
8. Frigidaire has done research on the effects of methanol in refrigerating systems. Frigidaire current practice is to use desiccants instead of methanol in the household refrigerating systems. Other products receive drier or methanol depending on economics and design requirements.

V. A. Williamitis
V. A. Williamitis
Materials & Process
Engineering Division

VAW:gmh

cc: G. R. Long
F. I. Payne
W. H. Smith
J. E. Dorn

SUMMARY OF SURVEY OF REFRIGERATION EQUIPMENT MANUFACTURERS, 3 MARCH 58

The following information was developed in accordance with directive of Mr. J. W. Millard, that survey conducted in 1956 be reviewed for current validity.

On 25 February, at 1600 hours, Mr. W. F. Kelly, E. I. DuPont, 40 North Street, N. Y., called in response to an inquiry submitted by Mr. Vogel to their local Office on a matter not germane to this memo. Mr. Kelly was asked whether the opinion of DuPont had changed from that expressed in their letter in report dated 3 February 1956. Mr. Kelly stated that DuPont still took the same stand in opposition to methanol, and added, without any knowledge of the motivation for the question, "In spite of what Kelvinator might say." He will gather together further documentation of DuPont's position and will give it to Mr. Vogel during his visit to N. Y. vicinity on 28 February 1958.

General Chemicals, Conetron Division, was contacted on 26 February 1958, and Mr. Madon stated that although some manufacturers believe that alcohol does no harm, Conetron opinion is that a dry system and a mechanical dryer is preferred. If the system moisture is kept below 25 ppm, alcohol will not be needed. If a system has alcohol and is later opened by a service man, additional alcohol may be added and would exceed the danger limits. They do not have firm information on what the danger limits are, but they are investigating at the University of Miami, and will forward such information as it is developed.

Mr. R. G. Grouch, Morge Plant, Muskegon Heights, Michigan, stated that the Morge position of 1956 is still firm. They are strictly opposed to the use of alcohol.

Mr. R. H. Smart, Sr., Carrier Corporation, Syracuse, N. Y., stated that Thamazone, a sodium alcohol compound, is slightly alkaline and therefore, not as potentially corrosive as methanol. However, no liquid desiccant is recommended. Tecumseh will allow Carrier to use alcohol under extremely careful quality control and moisture levels, but extra cost of such control would be prohibitive. At best, alcohol is undesirable since the safe limits could be exceeded by a mechanic on the first repair job. Carrier does not use it, although Mr. Smart said he had excellent success with it when he was with Kelvinator 25 years ago, and he believes they still use it. He believes it is used chiefly as a production cost consideration since it saves about 40¢ in materials alone per end item. He states that solid dryer had added advantage of removing acids somewhat, a function directly opposite that of methanol.

In conversation with Wendell Smith and Vic Williamitis of Frigidaire, Dayton, Ohio, they stated that in some applications, where a designed-in

pressure drop required compensation, they have obtained practical results using 3 cc's of methanol. They now only use methanol on one model horizontal food freezer, and in 1959 all their items will use mechanical dryers. They state that in all their failures of equipment using alcohol, they can identify corrosion stains on all defective items and approximately 5% of the failures can be attributed to iron-salt by-products of alcohol on the metals of the system. They are working on new dryers which will absorb prototype compounds and acids as well as water, a function that methanol cannot perform. They feel that 1 cc of alcohol will pick up an equal volume of water down to minus 10F, and that below this temperature, alcohol is ineffective. Although their dryer exceeds the cost of alcohol and a filter by about 15¢, they feel that in a period of over 10 years per item, without corrosion failure, the 15¢ is saved, but they cannot prove this except by their experience. Mr. Willmaritis stated that his personal opinion is that alcohol causes less damage while the equipment is running than it does in storage. The alcohol will tend to concentrate in the evaporator and during storage, when frozen flow has practically ceased, pin-point corrosion is bound to exist at the point where the alcohol/water concentrates in the evaporator. This is a particular hazard with the new Roll-Bond aluminum evaporators. If the corrosion should not completely penetrate the wall, the wall is weakened; also the corrosion by-products are a serious hazard. He feels that this storage condition would be of particular concern in Army use since the refrigerators are run before acceptance, and then they are often put into storage for extended periods.

No further effort will be made to secure additional information at this time since it would be a duplication of the work assignment which has been made to NBS. If the information obtained thus far can be considered to be representative of the industry, alcohol has very few advocates. Documentary evidence is on hand from various compressor manufacturers stating that use of alcohol will void compressor guarantees. The data to be furnished by DuPont as stated above was picked up by Mr. Vogel from Robert B. Sengsten, District Sales Supervisor, E. I. DuPont, De Nemours & Company, Inc., on 28 February. These documents are available for study and they support the above statements of Mr. Kelly. Mr. Sengsten stated that DuPont has evaluated over 200 different liquid additives and finds that their opinion is applicable to all of them.

PAUL E. J. VOGEL

Cy furnished:

JRMillard (Chf, LEO)

U. S. DEPARTMENT OF COMMERCE

Sinclair Weeks, *Secretary*

NATIONAL BUREAU OF STANDARDS

A. V. Astin, *Director*



THE NATIONAL BUREAU OF STANDARDS

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WASHINGTON, D. C.

Electricity and Electronics. Resistance and Reactance. Electron Devices. Electrical Instruments. Magnetic Measurements. Dielectrics. Engineering Electronics. Electronic Instrumentation. Electrochemistry.

Optics and Metrology. Photometry and Colorimetry. Optical Instruments. Photographic Technology. Length. Engineering Metrology.

Heat. Temperature Physics. Thermodynamics. Cryogenic Physics. Rheology. Engine Fuels. Free Radicals Research.

Atomic and Radiation Physics. Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics. Neutron Physics. Nuclear Physics. Radioactivity. X-rays. Betatron. Nucleonic Instrumentation. Radiological Equipment.

Chemistry. Organic Coatings. Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Molecular Structure and Properties of Gases. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

Mechanics. Sound. Mechanical Instruments. Fluid Mechanics. Engineering Mechanics. Mass and Scale. Capacity, Density, and Fluid Meters. Combustion Controls.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastics. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics.

Mineral Products. Engineering Ceramics. Glass. Refractories. Enameled Metals. Concreting Materials. Constitution and Microstructure.

Building Technology. Structural Engineering. Fire Protection. Air Conditioning, Heating, and Refrigeration. Floor, Roof, and Wall Coverings. Codes and Safety Standards. Heat Transfer.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics.

Data Processing Systems. SEAC Engineering Group. Components and Techniques. Digital Circuitry. Digital Systems. Analog Systems. Application Engineering.

• Office of Basic Instrumentation.

• Office of Weights and Measures.

BOULDER, COLORADO

Cryogenic Engineering. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

Radio Propagation Physics. Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services. Sun-Earth Relationships. VHF Research.

Radio Propagation Engineering. Data Reduction Instrumentation. Modulation Systems. Navigation Systems. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Radio Systems Application Engineering. Radio Meteorology.

Radio Standards. High Frequency Electrical Standards. Radio Broadcast Service. High Frequency Impedance Standards. Calibration Center. Microwave Physics. Microwave Circuit Standards.

